APPARATUS AND METHOD FOR DETECTING CHEMICAL AGENTS

BACKGROUND OF THE INVENTION

The present invention relates to an apparatus and a method for the detection of chemical agents, in particular, an apparatus and a method for the detection of chemical agents which are suitable for detecting 2,2'-dichloroethyl sulphide (hereinafter referred to as sulfur mustard) and 2-chlorovinyl-dichloroarsine (hereinafter referred to as lewisite 1) with a mass spectrometer by employing atmospheric pressure chemical ionization (APCI).

In recent years, there has been a desire for an apparatus for detecting chemical agents, for a countermeasure against chemical terrorism including the sarin case. A chemical agent is generally detected by its analysis, and examination by gas chromatography mass spectrometry (GC/MS) is a leading method for the detection. In general, the chemical agent itself is rarely detected in a sample and its presence is proved by detecting a decomposition product capable of remaining easily.

As a prior art regarding another apparatus for analyzing a chemical agent, liquid chromatography mass spectrometry (LC/MS) for the separation and analysis of a volatile or nonvolatile compound is known.

Fig. 14 is a diagram illustrating an outline of the structure of an analyzer according to a prior art, in which the liquid chromatography mass spectrometry is employed. The analyzer according to

5   the prior art is explained below. In Fig. 14, numeral 101 denotes a liquid chromatograph (LC), numeral 102 a connecting tube, numeral 103 an ion source, numeral 104 an electric source for ion source, numerals 105 and 109 signal cords, numeral 106 a mass spectrometry section,

10   numeral 107 a vacuum system, numeral 108 an ion detector, and numeral 110 a data processor.

As shown in Fig. 14, the analyzer according to the prior art, in which the liquid chromatography mass spectrometry is employed, comprises the liquid

15   chromatograph (LC) 101 for separating a sample solution into components, the ion source 103 for producing ions from sample molecules which is controlled by the electric source for ion source 104, the mass spectrometry section 106 for subjecting the produced

20   ions to mass spectrometry which is evacuated by the vacuum system 107, the ion detector 108 for detecting the ions subjected to the mass spectrometry, and the data processor 110 for processing data. The zone comprising the ion source 103, the mass spectrometry

25   section 106 and the ion detector 108 constitutes a mass spectrometry apparatus (MS).

In the above, the sample solution separated into components in the liquid chromatograph (LC) 101 is

introduced into the ion source 103 operated at
atmospheric pressure, through the connecting tube 102.
The ion source 103 is controlled by the electric source
for ion source 104 through the signal cord 105 and
5   produces ions from sample molecules in the sample
solution.   Then, the produced ions are introduced into
the mass spectrometry section 106 and subjected to mass
spectrometry.   The mass spectrometry section 106 has
been evacuated by the vacuum system 107.   The ions
10   subjected to the mass spectrometry are detected by the
ion detector 108.   The signals obtained by the
detection are sent to the data processor 110 through
the signal cord 109 to give analytical data such as a
mass spectrum or a chromatogram.
15   The mass spectrometry apparatus in the
analyzer composed as described above requires an
interface means between the mass spectrometry apparatus
and the liquid chromatograph (LC) 101 because ions have
to be treated in a vacuum in the apparatus.   That is,
20   LC is an apparatus in which a large volume of water or
an organic solvent is treated at atmospheric pressure,
while MS is an apparatus in which ions are treated in a
high vacuum.   Therefore, direct connection of these two
apparatus with each other has been considered
25   difficult.
          A method called Ion Mobility Spectrometry is
mainly a method comprising a combination of the
ionization of a sample by means of a radiation source

and the measurement of the mobility of ions in an electric field. This method is a leading method for on-the-spot detection, and many products employing this method have been produced in Europe and America. The

5 Ion Mobility Spectrometry method is often adopted for many purposes including military purposes because it permits miniaturization of a detector as compared with GC/MS and LC/MS. However, in Ion Mobility Spectrometry, a sample is not distinguished by mass-to-

10 charge ratio (mass number of ion/valence of ion), so that the display of a detection result is rough. Therefore, it is prescribed that soldiers have to carry a detector in order to wear a protective mask when an alarm is sounded.

15 As a prior art regarding the Ion Mobility Spectrometry method, there is known, for example, the technique disclosed in U.S. Patent 6,225,623 B1.

The prior arts described above involve the following problems. An electronic ionization (EI)

20 technique tends to decompose a substance to be detected because it applies a high energy to the substance itself. In a detecting apparatus employing GC/MS, ions having a molecular weight higher than that of a substance to be detected are difficult to monitor, so

25 that it is difficult to specify a sample. GC and LC treatments for separating a substance to be detected extend the detection time.

The Ion Mobility Spectrometry method does not

makes it possible to specify the kind of a chemical agent and is disadvantageous in that it responds to various compounds, resulting in difficult judgment on a sample to be subjected to detection and a high rate of

5 wrong information. As described above, when the Ion Mobility Spectrometry method is adopted, the sample is difficult to specify and the rate of wrong information is high.

An object of the present invention is to

10 solve such problems in the prior arts and provide an apparatus and a method for the detection of chemical agents which are suitable for detecting sulfur mustard and lewisite 1 and are satisfactory from the viewpoint of the speed of detection of chemical agents, the

15 reduction of the rate of wrong information, the specification of the kinds of the chemical agents, and an unmanned continuous-monitoring apparatus.

SUMMARY OF THE INVENTION

According to the present invention, the above

20 object can be achieved by providing an ion source into which a test sample is introduced and in which a preset temperature at which the test sample is positively or negatively ionized therein by corona discharge is 110°C to 180°C; and a mass spectrometry section where the

25 ions produced in said ion source are subjected to mass spectrometry, and by detecting signals due to a chemical agent to be detected.

In addition, the above object can be achieved by providing an ion source into which a test sample is introduced and in which a preset temperature at which the test sample is positively or negatively ionized
5   therein by corona discharge is 110°C to 180°C; a mass spectrometry section where the ions produced in said ion source are subjected to mass spectrometry; and a means for monitoring ionic strength due to a chemical agent to be detected.

10   Further, the above object can be achieved by providing an ion source into which a test sample is introduced and in which a preset temperature at which the test sample is positively or negatively ionized therein by corona discharge is 110°C to 180°C; a mass
15   spectrometry section where the ions produced in said ion source are subjected to mass spectrometry; and a means for monitoring the ionic strength of ions having mass-to-charge ratio (mass number of ion/valence of ion) values corresponding to a chemical agent to be
20   detected.

          Still further, the above object can be achieved by providing a sample introduction section into which a test sample is introduced and in which a preset temperature at which the test sample is heated
25   therein is 110°C to 180°C; an ion source where a preset temperature at which the gas produced by the heating is positively or negatively ionized therein by corona discharge is 110°C to 180°C; and a mass spectrometry

section where the ions produced in said ion source are subjected to mass spectrometry, and by detecting signals due to a chemical agent to be detected.

Still further, the above object can be achieved by providing a sample introduction section into which a test sample is introduced and in which a preset temperature at which the test sample is heated therein is 110°C to 180°C; an ion source where a preset temperature at which the gas produced by the heating is positively or negatively ionized therein by corona discharge is 110°C to 180°C; a mass spectrometry section where the ions produced in said ion source are subjected to mass spectrometry; and a means for monitoring ionic strength due to a chemical agent to be detected.

Still further, the above object can be achieved by providing a sample introduction section into which a test sample is introduced and in which a preset temperature at which the test sample is heated therein is 110°C to 180°C; an ion source where a preset temperature at which the gas produced by the heating is positively or negatively ionized therein by corona discharge is 110°C to 180°C; a mass spectrometry section where the ions produced in said ion source are subjected to mass spectrometry; and a means for monitoring the ionic strength of ions having mass-to-charge ratio (mass number of ion/valence of ion) values corresponding to a chemical agent to be detected.

In the above, the aforesaid ion source is constructed so as to employ backflow type atmospheric pressure chemical ionization (APCI) in which the test sample from the aforesaid sample introduction section

5   is introduced into a place between a corona discharge occurrence portion and the mass spectrometry section and flows toward the corona discharge occurrence portion opposite to the mass spectrometry section.

The present invention using the above-

10 mentioned means makes it possible to specify chemical agents and reduce the rate of wrong information and is suitable for detecting, in particular, sulfur mustard and lewisite 1. The detection of chemical agents employing the backflow type atmospheric pressure

15 chemical ionization (APCI), in which the test sample from the sample introduction section is introduced into a place between the corona discharge occurrence portion and the mass spectrometry section and flows toward the corona discharge occurrence portion opposite to the

20 mass spectrometry section, is characteristic of the present invention.

Other objects, features and advantages of the invention will become apparent from the following description of the embodiments of the invention taken

25 in conjunction with the accompanying drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a block diagram showing an outline

of the structure of an apparatus for detecting chemical agents according to one embodiment of the present invention.

Fig. 2 is a perspective view showing the appearance of the detecting apparatus according to the embodiment of the present invention.

Fig. 3 is a cross-sectional view showing an example of the structure of the filter paper heating section (an oven) shown in Fig. 2.

Fig. 4 is a block diagram showing examples of the structures of the ionization section and mass spectrometry section of the detecting apparatus according to the embodiment of the present invention.

Fig. 5 is a graph illustrating a mass spectrum of sulfur mustard obtained according to the embodiment of the present invention.

Fig. 6 is a graph illustrating characteristics at a sample introduction section temperature of 110°C and an ion source temperature of 110°C of signals at mass-to-charge ratio values of 123 and 158, respectively, detected by the introduction of sulfur mustard as a sample.

Fig. 7 is a graph illustrating characteristics at a sample introduction section temperature of 180°C and an ion source temperature of 150°C of signals at mass-to-charge ratio values of 123 and 158, respectively, detected by the introduction of sulfur mustard as a sample.

Fig. 8 is a graph illustrating the drift voltage dependence of a signal at a mass-to-charge ratio value of 123 detected by the introduction of sulfur mustard as a sample.

5   Fig. 9 is a graph illustrating a mass spectrum of lewisite 1 obtained according to the embodiment of the present invention.

Fig. 10 is a graph illustrating characteristics at a sample introduction section

10   temperature of 30°C and an ion source temperature of 110°C of signals at mass-to-charge ratio values of 187 and 205, respectively, detected by the introduction of lewisite 1 as a sample.

Fig. 11 is a graph illustrating

15   characteristics at a sample introduction section temperature of 110°C and an ion source temperature of 110°C of signals at mass-to-charge ratio values of 187 and 205, respectively, detected by the introduction of lewisite 1 as a sample.

20   Fig. 12 is a graph illustrating characteristics at a sample introduction section temperature of 180°C and an ion source temperature of 150°C of signals at mass-to-charge ratio values of 187 and 205, respectively, detected by the introduction of

25   lewisite 1 as a sample.

Fig. 13 is a graph illustrating the drift voltage dependence of signals at mass-to-charge ratio values of 187 and 205, respectively, detected by the

introduction of lewisite 1 as a sample.

Fig. 14 is a diagram illustrating an outline of the structure of an analyzer according to a prior art in which the liquid chromatography mass

5   spectrometry is employed.

DETAILED DESCRIPTION OF THE INVENTION

Embodiments of the apparatus and method for detecting chemical agents of the present invention are explained below in detail with reference to the

10   drawings.

Fig. 1 is a block diagram showing an outline of the structure of an apparatus for detecting chemical agents according to one embodiment of the present invention. In Fig. 1, numeral 1 denotes a sample

15   introduction section, numeral 2 an ionization section, numeral 3 a mass spectrometry section, numeral 4 a controller, numeral 5 a suction pump, numeral 6 a computer for instrumentation, numeral 7 a vacuum pump, and numeral 16 a sample.

20   As shown in Fig. 1, the apparatus for detecting chemical agents according to the embodiment of the present invention comprises the sample introduction section 1, the ionization section 2 as ion source, the mass spectrometry section 3, the controller

25   4, the suction pump 5, the computer for instrumentation 6 and the vacuum pump 7. In the thus constructed apparatus for detecting chemical agents, the sample 16

having fine particles of a hazardous material adhering thereto which has been introduced into the sample introduction section 1 is gasified by heating by a heating mechanism (not shown) provided in the sample

5 introduction section 1. The gasified sample is introduced into the ionization section 2 by a flow of the air 81 (shown by the thick line in Fig. 1) sucked by the suction pump 5. The suction pump 5 has a function of discharging the air sucked and a function

10 of making the volume of the air sucked variable in the range of 0 to 2 liters/min by means of a mass flow controller.

The test sample introduced into the ionization section 2 as ion source is sent to a corona

15 discharge region at the pointed end of the cat whisker for corona discharge described hereinafter, and is positively ionized depending on the kinds of one or more components to be detected, by a high positive voltage (approximately 2 kV to 5 kV) applied to the cat

20 whisker. Only the positively ionized component(s) are introduced into the mass spectrometry section 3 through a first small hole provided in the ionization section 2, by an electric field applied to the region extending from the ionization section 2 to the mass spectrometry

25 section 3. In this case, surplus substances other than ions and molecules which pass through the first small hole in the ionization section 2 are discharged from the ionization section 2 by the suction pump 5 and then

discharged from the apparatus. The adsorption of the

sample on the inner wall of a path for sample

introduction between the sample introduction section 1

and the ionization section 2 and on the inside of the

5   ionization section 2 can be prevented by maintaining

the path for sample introduction and the ionization

section 2 at a high temperature.

The ions introduced into the mass

spectrometry section 3 pass through a differential

10   exhaust portion in the mass spectrometry section 3

evacuated by the vacuum pump 7, and they are converged

by an electrostatic lens system and then subjected to

mass spectrometry with a mass spectrometer. The vacuum

pump 7 also has a function of keeping the inside of a

15   chamber accommodating the mass spectrometer, at a high

vacuum. The ions picked out by the mass spectrometer

are converted to electrons by a secondary-electron

multiplier in the mass spectrometry section 3, and the

current signals thus obtained are amplified by an

20   amplifier and then sent to the computer for

instrumentation 6.

The computer for instrumentation 6 conditions

the signals input from the mass spectrometry section 3

and displays, for example, the relationship between

25   mass number/electric charge (mass-to-charge ratio) and

ionic strength (mass spectrum), or the change with time

of ionic strength at a certain mass-to-charge ratio

(mass chromatogram). The final display may be not the

above-mentioned mass spectrum or mass chromatogram, but a further simplified display. That is, when the apparatus for detecting chemical agents according to the embodiment of the present invention is used as an apparatus for detecting hazardous materials, it is sufficient that only whether an undesirable chemical agent has been detected or not is displayed.

The controller 4 performs on/off control of the functional sections constituting the detecting apparatus, setting of temperature/voltage/vacuum pressure, status monitoring, and the like. Such connections are indicated by the control signal, data 82 shown by the thin lines in Fig. 1.

As described above, according to the embodiment of the present invention, it becomes possible to analyze fine particles of a hazardous material adhering to the sample 16 introduced into the sample introduction section 1, in the mass spectrometry section 3.

Fig. 2 is a perspective view showing the appearance of the detecting apparatus according to the embodiment of the present invention. As shown in Fig. 2, the detecting apparatus is composed of a filter paper heating section 21 having a filter paper inlet 20, an analysis section 22 and a display section 23, and can be moved owing to wheels located in the lowermost part of the apparatus.

During the production or transportation of a

chemical agent, a very slight amount of the chemical

agent usually adheres to the hands, skin, clothes and

the like of a person who is handling the chemical

agent. When this person handles his or her personal

5   effects such as a bag, the chemical agent adheres also

to the personal effects.

        Therefore, in the embodiment of the present

invention, the surface of, for example, a bag as an

object of examination (a substance subjected to

10   detection) is wiped with a clean and soft material

(e.g. cloth or filter paper) (which is hereinafter

referred to as test paper but needs not always be

paper), and a chemical agent adhering to the test paper

is analyzed. That is, the test paper having the

15   chemical agent adhering thereto is inserted into the

filter paper heating section 21 through the filter

paper inlet 20. Since the test paper is heated in the

filter paper heating section 21, the chemical agent

adhering to the test paper is vaporized, and then

20   analyzed by the analysis section 22. The analysis

section is accommodating the detecting apparatus having

the structure explained with reference to Fig. 1 and is

equipped with a database in which information

concerning signals due to the chemical agent has been

25   registered. When the detection of predetermined

signals characteristic of the chemical agent is

confirmed by the analysis result and the information

registered in the database, the computer for

instrumentation 6 displays a warning in the display
section 23.

Fig. 3 is a cross-sectional view showing an
example of the structure of the filter paper heating
5   section (an oven) shown in Fig. 2. In Fig. 3, numeral
24 denotes a filter paper, numeral 25 a tray, numeral
25' a grip, numeral 26 a tray holder, numeral 27 a
sensor, numeral 28 a halogen lamp, numeral 29 an air
inlet tube, numeral 30 a filter, numeral 31 a sample
10 inlet tube, and numeral 32 a cover.

The filter paper heating section (the oven)
21 is composed of the tray holder 26, the halogen lamp
28 provided as a heat source in the tray holder 26, and
the tray 25 on which the filter paper 24 is set. In
15 the filter paper heating section 21 thus composed, the
filter paper 24, a test paper with which an object of
examination has been wiped is set on the tray 25 of
slide type at first. The tray 25 having the filter
paper 24 set thereon is inserted into the tray holder
20 26. When the sensor 27 senses that the tray 25 has
been inserted to be set in a predetermined position,
the halogen lamp provided in the upper part of the tray
holder 26 is lighted. The filter paper 24 is heated by
heat rays from the halogen lamp 28, and materials
25 adhering to the filter paper 24 are vaporized. The
heating temperature is preferably 100°C or higher. The
sample thus produced from the filter paper 24 is sent
to the analysis section 22 through the sample inlet

tube 31 together with air introduced into the tray
holder 26 through the air inlet tube 29.

The air inlet tube 29 is preferably equipped
with the filter 30 for removing dust and the like. For
5 safety, the filter paper heating section 21 is
preferably equipped with the cover 32 and the grip 25'
which have thermal insulating properties, because its
temperature becomes high. The sample introduction
section 1 may be such that a test sample (a substance
10 to be subjected to detection) sucked from the outside
is directly introduced into the ionization section 2.

Fig. 4 is a block diagram showing examples of
the structures of the ionization section and mass
spectrometry section of the detecting apparatus
15 according to the embodiment of the present invention.
In Fig. 4, numeral 33 denotes a cat whisker, numeral 34
a counter electrode, numeral 35 an opening, numeral 36
a suction pump, numerals 37a and 37b small-hole-
provided electrodes, numeral 38a a first small hole for
20 ion introduction, numeral 38b a second small hole for
ion introduction, numeral 39 a differential exhaust
portion, numerals 40a and 40b exhaust systems, numeral
41 a vacuum portion, numerals 42a and 42b end cap
electrodes, numeral 43 an ion-converging lens, numeral
25 44 a ring electrode, numeral 45 a quartz ring, numeral
46 a gas feeder, numeral 47 a gas inlet tube, numeral
48 a gate electrode, numeral 49 a conversion electrode,
numeral 50 a scintillator, numeral 51 a

photomultiplier, and numeral 52 a data processor.

In Fig. 4, the cat whisker 33 is located in the ionization section 2, and a high voltage is applied between the cat whisker 33 and the counter electrode

5   34. By this application, corona discharge is caused near the pointed end of the cat whisker 33, so that nitrogen, oxygen, water vapor and the like are ionized at first. The ions thus formed are called primary ions. The primary ions move toward the counter

10 electrode 34 owing to an electric field. The test sample supplied from the sample introduction section to the region between the counter electrode 34 and the small-hole-provided electrode 37a through the sample inlet tube 31 flows toward the cat whisker 33 through

15 the opening 35 provided in the counter electrode 34 in the ionization section 2, owing to the suction pump 36, and is ionized by reaction with the primary ions.
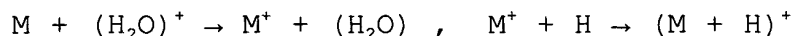
There is an electric potential difference of about 1 kV between the counter electrode 34 and the

20 small-hole-provided electrode 37a. Therefore, the ions formed by the reaction move toward the small-hole-provided electrode 37a and are introduced into the differential exhaust portion 39 through the small hole 38a. Adiabatic expansion takes place in the

25 differential exhaust portion 39, resulting in so-called clustering, i.e., the adhesion of solvent molecules and the like to the ions. For reducing the clustering, the small-hole- provided electrodes 37a and 37b are

preferably heated with a heater or the like.

When the ionization section 2 having the
structure shown in Fig. 4 is used, the primary ions
formed by the corona discharge move toward the counter
5   electrode 34 owing to the electric potential difference
between the cat whisker 33 and the counter electrode 34
and then move toward the small-hole-provided electrode
37a through the opening 35. Since the test sample from
the sample introduction section is supplied to the
10   region between the counter electrode 34 and the small-
hole-provided electrode 37a, the reaction of the
primary ions with the test sample takes place. Neutral
molecules and the like produced by the corona discharge
flow toward the cat whisker 33 from the counter
15   electrode 34 owing to the suction pump 36 and hence are
removed from the corona discharge portion. In
addition, the neutral molecules and the like hardly
flow into the region where the ionization reaction
between the primary ions and the sample takes place.
20   By thus separating the region for the formation of the
primary ions by the corona discharge and the region for
the ionization reaction between the primary ions and
the sample to prevent the radical neutral molecules
produced by the corona discharge from flowing into the
25   ionization region, the decomposition of the sample in
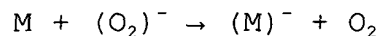the ionization region can be reduced.

As described above, in the embodiment of the
present invention, the primary ions are formed by

utilizing the corona discharge in the air and the test
sample is ionized by utilizing the chemical reaction of
the primary ions with the test sample. This method is
called an atmospheric pressure chemical ionization

5   method. In the case of sulfur mustard, there is
employed a positive ionization mode in which positive
ions are formed by applying a high positive voltage to
the cat whisker 33. In this case, the primary ions are
often ions of water molecules [$(H_2O)^+$]. A typical

10   positive ionization reaction can be represented by the
following formulas:

$$M + (H_2O)^+ \rightarrow M^+ + (H_2O) \quad , \quad M^+ + H \rightarrow (M + H)^+$$

15   wherein M is a molecule of a substance to be detected
and H is a hydrogen atom.

In the case of lewisite 1, there is employed
a negative ionization mode in which negative ions are
formed by applying a high negative voltage to the cat

20   whisker 33. In this case, the primary ions are often
ions of oxygen molecules [$(O_2)^-$]. A typical negative
ionization reaction is shown below:

$$M + (O_2)^- \rightarrow (M)^- + O_2$$

wherein M is a molecule in a gas.

25   The ions formed as described above are
introduced into the vacuum portion 41 evacuated by the

exhaust system 40b, through the first small hole for
ion introduction 38a of the small-hole-provided
electrode 37a, the differential exhaust portion 39
evacuated by the exhaust system 40a, and the second
5   small hole for ion introduction 38b of the small-hole-
provided electrode 37b. A voltage called a drift
voltage is applied between the small-hole-provided
electrodes 37a and 37b. This drift voltage is
effective in improving the ion permeability of the
10   second small hole for ion introduction 38b by drifting
the ions introduced into the differential exhaust
portion 39, toward the small hole for ion introduction
38b, and is effective also in releasing solvent (e.g.
water) molecules adhering to the ions, by collision
15   between the ions and gas molecules remaining in the
differential exhaust portion 39. A voltage is further
applied to the small-hole-provided electrode 37b. This
voltage affects energy at the time of passage of the
ions through the opening provided in the end cap
20   electrode 42a (incident energy).

     Since the efficiency of ion trapping of an
ion trap mass spectrometer used in the embodiment of
the present invention is dependent on the incident
energy of the ions, the above-mentioned voltage is set
25   so as to improve the efficiency of trapping. The ions
introduced into the vacuum portion 41 are converged by
the ion-converging lens 43 and then introduced into the
ion trap mass spectrometer composed of the end cap

electrodes 42a and 42b and the ring electrode 44. The

end cap electrodes 42a and 42b and the ring electrode

44 are held by the quartz ring 45.

A gas for collision such as helium is

5   introduced into the mass spectrometer from the gas

feeder 46 through the gas inlet tube 47. The gate

electrode 48 is provided in order to control the timing

of introduction of the ions into the ion trap mass

spectrometer. The ions discharged from the mass

10 spectrometer after mass spectrometry are detected by a

detector composed of the conversion electrode 49, the

scintillator 50 and the photomultiplier 51. The ions

collide with the conversion electrode 49 to which a

voltage for accelerating the ions is being applied.

15 Charged particles are liberated from the surface of the

conversion electrode 49 by the collision of the ions

with the conversion electrode 49. The charged

particles are detected by the scintillator 50 and the

resulting signals are amplified by the photomultiplier

20 51. The signals detected are sent to the data

processor 52. Although an explanation is given above

by taking the case where the ion trap mass spectrometer

is used, a quadrupole mass spectrometer may be used.

The data processor 52 identifies ions having

25 mass-to-charge ratio values corresponding to a chemical

agent to be detected (for example, positive ions having

mass-to-charge ratio values corresponding to sulfur

mustard, or negative ions having mass-to-charge ratio

values corresponding to lewisite 1), and determines the
signal strength due to the ions to judge whether the
chemical agent to be detected, i.e., sulfur mustard or
lewisite 1 has been detected or not. When sulfur

5   mustard or lewisite 1 has been detected, the data
processor 52 displays both a warning and the kind of
the detected chemical agent in the display section 23.
The warning may be given also by giving a loud sound or
switching on and off a red warning lamp, in order to

10   attract attention.

Fig. 5 is a graph illustrating a mass
spectrum of sulfur mustard obtained according to the
embodiment of the present invention. The graph is
obtained when sulfur mustard vapor is directly

15   introduced into the sample introduction section and the
following conditions are employed: the detection of
positive ions, a drift voltage of 50 V, a temperature
of the ionization section of 150°C, and a temperature
of the sample introduction section of 180°C.

20   In this case, as shown in Fig. 5, signals at
mass-to-charge ratio values of 123 and 158,
respectively, were detected. Since sulfur mustard has
a molecular weight M_{HD} of 158 or 160, the signal at a
mass-to-charge ratio value of 123 is due to $(M_{HD} - Cl)^+$

25   and the signal at a mass-to-charge ratio value of 158
is due to $(M_{HD})^+$. That is, when both of the signals at
mass-to-charge ratio values of 123 and 158 are
detected, it is judged that sulfur mustard has been

detected. The above detection method can reduce the rate of wrong information. When only the signal at a mass-to-charge ratio value of 123 (or 158) is detected in the case where another component gives the signal at

5 a mass-to-charge ratio value of 123 (or 158) by accident, judgment that sulfur mustard has been detected gives wrong information in some cases.

Figs. 6 and 7 are graphs illustrating the temperature dependence of signals at mass-to-charge

10 ratio values of 123 and 158, respectively, detected by the introduction of sulfur mustard as a sample. The case shown in Fig. 6 is the changes with time of ionic strength signal level at a sample introduction section temperature of 110°C and an ion source temperature of

15 110°C observed when sulfur mustard gas is sucked for a definite time and then the sucking is stopped. The sample introduction section was composed of a SUS piping having a temperature-controlling ability. The case shown in Fig. 7 is the changes with time of ionic

20 strength signal level at a sample introduction section temperature of 180°C and an ion source temperature of 150°C observed when sulfur mustard gas is sucked for a definite time and then the sucking is stopped. The sample introduction section was composed of a SUS

25 piping having a temperature-controlling ability.

When the sample introduction section and the ion source are set at high temperatures, respectively, there is a possibility that the adsorption of the

sample might be reduced, resulting in faster arrival of sulfur mustard gas at the ion source. The setting at high temperatures is effective in reducing the signal level rising time extending from the gas suction to the

5 signal detection, and in reducing the signal level dropping time extending from the stopping of the gas suction to the return of the signal level to the background level.

Fig. 8 is a graph illustrating the drift

10 voltage dependence of a signal at a mass-to-charge ratio value of 123 detected by the introduction of sulfur mustard as a sample. As can be seen from Fig. 8, a signal level higher than the background level can be attained at a drift voltage of not more than 80 V

15 and more than 40 V. The term "background level" means the level of a signal at a mass-to-charge ratio value of 123 attained when no sulfur mustard is introduced as a sample. Whether sulfur mustard has been detected or not is judged by monitoring signals on a level higher

20 than the background level. Accordingly, a higher signal level can be attained by setting the drift voltage at 50 V to 80 V.

Fig. 9 is a graph illustrating a mass spectrum of lewisite 1 obtained according to the

25 embodiment of the present invention. The graph is obtained when lewisite 1 vapor is directly introduced into the sample introduction section and the following conditions are employed: the detection of negative

ions, a drift voltage of -40 V, a temperature of the ionization section of 180°C, and a temperature of the sample introduction section of 180°C.

In this case, as shown in Fig. 9, signals at mass-to-charge ratio values of 187 and 205, respectively, were detected. Since lewisite 1 has a molecular weight M_L of 206 or 208, the signal at a mass-to-charge ratio value of 205 is due to $(M_L - H)^+$ and the signal at a mass-to-charge ratio value of 187 is due to a decomposition product of lewisite 1. That is, when both of the signals at mass-to-charge ratio values of 187 and 205 are detected, it is judged that lewisite 1 has been detected. The above detection method can reduce the rate of wrong information. When only the signal at a mass-to-charge ratio value of 187 (or 205) is detected in the case where another component gives the signal at a mass-to-charge ratio value of 187 (or 205) by accident, judgment that lewisite 1 has been detected gives wrong information in some cases.

Figs. 10 to 12 are graphs illustrating the temperature dependence of signals at mass-to-charge ratio values of 187 and 205, respectively, detected by the introduction of lewisite 1 as a sample. The case shown in Fig. 10 is the change with time of ionic strength signal level at a sample introduction section temperature of 30°C and an ion source temperature of 110°C observed when lewisite 1 gas is sucked for a definite time and then the sucking is stopped. The

sample introduction section was composed of a Teflon (a registered trade name) piping. The case shown in Fig. 11 is the changes with time of ionic strength signal level at a sample introduction section temperature of 110°C and an ion source temperature of 110°C observed when lewisite 1 gas is sucked for a definite time and then the sucking is stopped. The sample introduction section was composed of a SUS piping having a temperature-controlling ability. The case shown in Fig. 12 is the changes with time of ionic strength signal level at a sample introduction section temperature of 180°C and an ion source temperature of 150°C observed when lewisite 1 gas is sucked for a definite time and then the sucking is stopped. The sample introduction section was composed of a SUS piping having a temperature-controlling ability.

When the sample introduction section and the ion source are set at high temperatures, respectively, there is a possibility that the adsorption of the sample might be reduced, resulting in faster arrival of lewisite 1 gas at the ion source. The setting at high temperatures is effective in reducing the signal level rising time extending from the gas suction to the signal detection, and in reducing the signal level dropping time extending from the stopping of the gas suction to the return of the signal level to the background level.

Fig. 13 is a graph illustrating the drift

voltage dependence of signals at mass-to-charge ratio
values of 187 and 205, respectively, detected by the
introduction of lewisite 1 as a sample. As can be seen
from Fig. 13, a signal level higher than the background
5 level can be attained at a drift voltage in the range
of -30 V to -60 V. The term "background level" means
the level of signals at mass-to-charge ratio values of
187 and 205 attained in the case where no lewisite 1 is
introduced as a sample. Whether lewisite 1 has been
10 detected or not is judged by monitoring signals on a
level higher than the background level. Accordingly, a
higher signal level can be attained by setting the
drift voltage at -30 V to -60 V.

As explained above, according to the present
15 invention, the presence of sulfur mustard or lewisite 1
can easily be judged by sucking a test sample and
confirming mass-to-charge ratio in the analysis section
of the detecting apparatus [atmospheric pressure
chemical ionization (APCI) - mass spectrometer (MS)].

20 It should be further understood by those
skilled in the art that although the foregoing
description has been made on embodiments of the
invention, the invention is not limited thereto and
various changes and modifications may be made without
25 departing from the spirit of the invention and the
scope of the appended claims.